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28 APR 1967

525 298

No. 756,190



ISSUED Apr. 4, 1967
CLASS 401-54

CANADIAN PATENT

CROSSLINKED POLYETHERS

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Granted to Union Carbide Corporation, New York, New York,
U.S.A.

APPLICATION No. 934,887
FILED July 2, 1965
PRIORITY DATE Dec. 17, 1964 (419,196) U.S.A.

No. OF CLAIMS 6 - No drawing

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA.
RG-401-4-3

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CROSSLINKED POLYETHERS

This invention relates to chemically crosslinked polyethers. In a particular aspect, this invention is concerned with a process for chemically crosslinking polyethers with divinyl monomers in the presence of free radical catalysts, and to the crosslinked polymers prepared thereby.

In the present state of the art polyethers are not known to be amenable to crosslinking through carbon to carbon bonding by chemicals means. It is known that polyethers such as
10 poly(ethylene oxide) can be crosslinked readily through irradiation with gamma rays, however, heretofore, it has not been possible to crosslink polyethers via chemical means. Poly-(ethylene oxide) has been shown to form a crosslinked polymer of varying properties through irradiation with gamma rays such as those emitted by a cobalt 60 source. The properties of these irradiated poly(ethylene oxides) are highly dependent on the irradiation dose, that is, the irradiated poly(ethylene oxide) may range in properties from a soluble polymer with properties similar to the irradiated polymer, to a highly crosslinked horny
20 solid, insoluble in any solvent. Moreover, since gamma radiation involves the use of a potentially dangerous source with costly protective measures involved in its use, it is not the most desirable process for crosslinking polyethers.

It has now been found that polyethers can be successfully and readily crosslinked by a chemical process. This chemical process involves a rather simple chemical reaction and does not require a source of gamma radiation. The process of the present invention comprises chemically crosslinking polyethers with small amounts of divinyl monomers in the presence of a free radical
30 catalyst. The degree of crosslinking can be varied over a very



broad range. It is believed that the chemically crosslinked polymers of this invention may be more economically attractive than the radiation induced crosslinked polymers. The crosslinked polyethers of this invention are of particular interest in agricultural applications and in modifying film properties.

The novel process of this invention for crosslinking polyethers is believed to be accomplished through the grafting of a divinyl substituent of a divinyl monomer to the carbon atoms adjacent to the oxygen atom in the polyether chains. With
10 polyethers, it appears that the hydrocarbons on carbon atoms adjacent to the oxygen atom are rather labile and apparently are abstracted by free radical catalysts. These reactive sites then apparently react with a vinyl group if one is available and a grafting operation is complete. If this process is conducted with the right kind of a divinyl monomer as disclosed herein, then a crosslinked material is obtained. It is a requirement of the process of this invention that a divinyl monomer with its
20 divinyl substituents be used otherwise the crosslinking phenomenon will not occur. Monovinyl monomers will not crosslink as disclosed herein and, therefore, are not within the purview of this invention.

Accordingly, an object of the present invention is to provide a novel chemical process for crosslinking polyethers with a divinyl monomer in the presence of a free radical catalyst. Another object is to provide a novel process for chemically crosslinking poly(ethylene oxide) with a divinyl monomer in the presence of a free radical catalyst. A further object is to provide a process for chemically crosslinking poly(ethylene oxide) with methylenebisacrylamide in the presence of azobisisobutyro-
30 nitrile. A still further object is to provide novel crosslinked

polymers prepared by chemically crosslinking a polyether with a divinyl monomer in the presence of a free radical catalyst.

Another further object is to provide novel crosslinked polymers prepared by chemically crosslinking poly(ethylene oxide) with a divinyl monomer in the presence of a free radical catalyst.

Another object is to provide novel crosslinked polymers prepared as disclosed herein which find agricultural and microbiological uses as well as applications in modifying films. These and other objects of this invention will become apparent to those skilled in the art to which this invention pertains from the ensuing description thereof.

In general, several methods may be used in carrying out the crosslinking reaction of this invention. For either high, or low molecular weight polyethers, such as poly(ethylene glycol), known in the trade as Carbowax 6000, the reaction may be conducted in a stirred reaction flask merely by mixing, e.g., the low molecular weight poly(ethylene glycol) with the divinyl monomer and catalyst. For this method it is essential that the reaction temperature be high enough to allow the components to mix freely, and therefore should be above the melting point of the low molecular weight poly(ethylene glycol).

In another method, with either a high or low molecular weight polyether, the reaction may be conducted in a standard laboratory press. The catalyst and divinyl monomer crosslinking agent are intimately dispersed in the polyether. The resultant powder or mixture is then subjected to heat and pressure for a period of time and a thin crosslinked polyether plaque is obtained.

In a still further method, the polyether to be cross-linked may be extruded through a hot zone in the presence of the divinyl monomer crosslinking agent and catalyst. This method is

especially useful in a continuous operation.

The polyethers which can be chemically crosslinked according to this invention include a wide variety of known polyethers. It is believed that any polyether with a hydrogen atom on the carbon atom adjacent to the ether oxygen can be crosslinked as disclosed herein. Among the polyethers which may be crosslinked according to this invention include poly(alkylene oxides) such as poly(ethylene oxide), poly(propylene oxide), and mixtures thereof; polyvinyl ethers such as polyvinyl isobutyl
10 ether; poly(alkylene glycols) such as poly(ethylene glycol), poly(propylene glycol); and poly(styrene oxide); and mixtures of different poly(alkylene oxides), polyvinyl ethers, and poly-(alkylene glycols) with themselves and each other. In general, polyethers having an average molecular weight of 5,000 to 5,000,000 or greater, up to 10,000,000, are operable. This invention is particularly adapted to the chemical crosslinking of poly(ethylene oxide) but is in no way restricted thereto.

The highest degree of crosslinking has been obtained with molten polyethers, or very high concentrated solutions of
20 polyethers. It appears that most efficient crosslinking occurs with a non-crystalline polyether, that is, with melted polyethers or solutions of polyethers. The success of the crosslinking reaction is observed in the resulting polyether's solubility. Insolubility in water is taken as the criterion for a successful crosslinking reaction in the process of this invention, e.g., insolubility of crosslinked poly(ethylene oxide) in water.

The divinyl monomers which are suitable in the practice of this invention include divinyl benzene, divinyl adipate, and other divinyl esters; ethylene glycol dimethacrylate, and other
30 dimethacrylates; and diacrylates, methylenebisacrylamide, and others.

Of course, mixtures and various combinations of the aforementioned divinyl monomers are also suitable. The preferred divinyl monomer for crosslinking poly(ethylene oxide) is methylenebisacrylamide.

The relative amounts of polyether and divinyl monomer employed in the process of this invention can be varied over a wide range. It has been found that the higher the molecular weight of the polyether, the less divinyl monomer is required to obtain crosslinking, as indicated by the insolubility of the resultant polymer. In general, the amount of divinyl monomer required will represent from 0.2 to 10 per cent of the amount of polyether employed. Ideally, if a polymer is completely crosslinked to an infinite network, i.e., only a single molecule exists, then the polymer will be insoluble in water. Different degrees of crosslinking can be measured roughly by the amount of swelling or adsorption in a good solvent for the linear polymer. In the present invention, crosslinking is determined by the solubility of the resulting polymer in water, or some other solvent for the original polyether. Other solvents are acetonitrile, methylene dichloride, ethylene dichloride.

A number of different free radical catalysts can be used in the process of this invention. Typical free radical catalysts include azobisisobutyronitrile, benzoyl peroxide, acetyl peroxide, 2,4-dichlorobenzoyl peroxide, and in general any free radical generating compound which will generate a substantial number of free radicals over a temperature range of interest from about 65 to about 150°C. The preferred free radical catalyst for poly-(ethylene oxide) is azobisisobutyronitrile. The amount of catalyst may vary from 0.1 to about 5.0 per cent based on the total amount of divinyl monomer plus polyether.

The temperature at which the process can be carried out is, of course, related to the particular catalyst used in the reaction. The preferred temperature range for crosslinking

poly(ethylene oxide) is from about 75 to about 150°C. The preferred temperature is from about 100 to 125°C., particularly when using azobisisobutyronitrile as catalyst.

The following examples and tables will more fully illustrate the process and crosslinked polymers of this invention.

EXAMPLE 1

To a 500 ml. 4 neck reaction flask equipped with air driven stirrer, thermometer and nitrogen purge the following was added: 40 grams "Carbowax" 6000 [poly(ethylene glycol) of approximately 6000 molecular weight], 5 gms. divinyl adipate, 0.5 gms. 2,2'-azobis(2-methyl propionitrile). The poly(ethylene glycol) and divinyl adipate were added first, heated to 70-75°C. and then the catalyst was added. The agitation then had to be terminated within 1-2 minutes because gel formation prevented further stirring.

The product (approximately 45 gms.) was collected. 5 Gms. sample of the material was then dispersed in 100 ml. of water. Even after 5 days agitation, 1.3 gms. of the same were insoluble which represented 26 per cent of the sample. A sample of unreacted Carbowax 6000 was completely soluble.

Table I and II shows the crosslinking of various polyethers according to this invention. The procedure for Examples 2-10 was conducted in the same manner as Example 1. In Tables I and II, the poly(ethylene glycols) have molecular weights of approximately 6000 and 20,000, and the poly(ethylene oxides) have a molecular weight in excess of 100,000.

TABLE I

CROSSLINKING OF POLYETHERS BY GRAFTING

Example	Polyether	Divinyl Adipate %	Catalyst, % (Azobisiso- butyronitrile)	Temperature, °C.	% Insoluble Polyether in Water
2	90% Poly(ethylene glycol) 6000	9	1	75	22
3	90% Poly(ethylene glycol) 20,000	9	1	75	60
4	95% Poly(ethylene glycol) 20,000	4	1	75	62

TABLE II

CROSSLINKING OF POLYETHERS BY GRAFTING

Example	Polyether	Divinyl Adipate %	Catalyst, % (Azobisiso- butyronitrile)	Temperature, °C.	% Insoluble Polyether in Water
5	93% Poly(ethylene oxide)	5	2	75	10
6	93% Poly(ethylene oxide)	5	2	100	57
7	93% Poly(ethylene oxide)	5	2	125	67
8	88% Poly(ethylene oxide)	10	2	75	59
9	88% Poly(ethylene oxide)	10	2	100	64
10	88% Poly(ethylene oxide)	10	2	125	87

EXAMPLES 11-30

In these Examples, Table III, catalyst and crosslinking agent were dispersed in poly(ethylene oxide) simply by dissolving the catalyst in acetone, and the crosslinking agent in methanol, mixing them together and then mixing small amounts of this solution with the finely dispersed poly(ethylene oxide). The poly(ethylene oxide) was then evacuated under high vacuum to distill the solvents off the poly(ethylene oxide). The dried crosslinked poly(ethylene oxide) was then subjected to molding conditions.

- 10 To mold films, only 2 gms. of sample was needed. A Carver Laboratory press was used to mold thin plaques between sheets of aluminum foil. The solubility of the films was then determined in water at a polyether weight concentration of 5 per cent. Table III indicates the results obtained.

TABLE III
CROSSLINKING OF POLY(ETHYLENE OXIDE) BY GRAFTING

Example	Poly(ethylene oxide)*	N,N'-Methylene-bisacrylamide	Catalyst % azobisisobutyronitrile	Temperature °C.	% Water-Insoluble Polyether
11	96.75%	1.25%	2.0	75	90
12	96.75	1.25	2.0	100	50
13	96.75	1.25	2.0	125	55
14	96.75	1.25	2.0	150	50
15	96.5	2.5	1.0	75	70
16	96.5	2.5	1.0	100	65
17	96.5	2.5	1.0	125	55
18	96.5	2.5	1.0	150	55
19	97.75	1.25	1.0	75	65
20	97.75	1.25	1.0	100	60
21	97.75	1.25	1.0	125	50
22	97.75	1.25	1.0	150	55
23	98.4	0.6	1.0	75	soluble
24	98.4	0.6	1.0	100	50
25	98.4	0.6	1.0	125	45
26	98.4	0.6	1.0	150	20
27	98.3	1.2	0.5	75	soluble
28	98.3	1.2	0.5	100	60
29	98.3	1.2	0.5	125	75
30	98.3	1.2	0.5	150	50

* poly(ethylene oxide) average molecular weight of greater than 100,000.

Crosslinked polyethers of this invention are of particular interest in agricultural applications and in modifying films. They can be used as plant growth media with soil, sand, peat moss and/or vermiculite. The growth media which comprise the crosslinked polyethers and natural growth media, can also include active agents such as fertilizers, herbicides, fungicides and/or insecticides.

10 The crosslinked polyethers of this invention are believed to be structurally a matrix of crosslinked polyethers which are substantially insoluble in water, and organic solvents at ambient or elevated temperature; they will swell upon contact with liquids, solutions and/or suspensions into the polymeric matrix of the material; they will retain liquids and solutions incorporated into their matrix and will release the same to an environment which has a lower concentration of such liquids or solutions than that concentration of the liquid or solution within the polymeric matrix; they will incorporate liquids and solutions from the surrounding environment when the concentration of such liquids and solutions in the surrounding environment is greater
20 than the concentration of the same within their polymeric matrix and the liquids and solutions are releasable from the polymeric matrix by evaporation.

Plants can be rendered more resistant to moisture stress by contacting the roots with an aqueous slurry of one of the crosslinked polyethers of this invention. The crosslinked polyethers can be admixed or mulched with the soil in dry or substantially dewatered condition along with substantially dry active agents such as fertilizers, herbicides, nematocides, and insecticides. Upon application of water to the soil the active
30 agents will be solubilized and the water and active agents will

be sorbed by the polymeric matrix. Again, the problem of excessive loss of water by evaporation or by loss to the natural water table and loss of the active agents by leaching is obviated. Also, because the activating carrier is able to sorb moisture from the so-called dry soils, activation of active agents will begin without additional rainfall.

A particular and distinct advantage of the present growth medium containing crosslinked polyethers and soil and so forth, is the manner in which the plant roots can make use of the crosslinked polymeric material. The plant roots can grow into the crosslinked polymeric matrix itself and thereby come into direct contact with water and the other active agents incorporated within the polymeric matrix. The ability of the plant roots to grow into the polymeric matrix permits more efficient utilization of water and other active agents because the water and active agents are directly contacted by the roots. Also, plants whose roots grow into the polymeric matrix, thereby causing the crosslinked polymeric matrix to cling to the plant roots, are much more resistant to extended periods of moisture stress.

The term "moisture stress" is defined herein to mean a situation wherein the internal moisture of the plant is transpired or evaporated at a rate greater than the rate which water enters the plant. The latter rate is due primarily to the lack of available moisture. There is much less destruction of seedlings during shipping and transplanting operations with such plants as tobacco, tomatoes, strawberries, annuals, and perennials, holding perennials, woody plants, ornamentals and seedlings when grown in the soil crosslinked polymeric formulations of the present invention.

There are many instances wherein the insoluble cross-linked polyester matrix containing water and/or fertilizer or

other active agents can be an ideal growth medium for germination of seeds and/or rooting of plant cuttings. The seeds of beans, lettuce, tomatoes, peppers, petunias, pansies, marigolds, and snap dragons, can be germinated in the crosslinked polymeric matrix-water media.

The crosslinked polyethers are not consumed to any significant extent by the plants themselves, but act as inert components in the growth medium or as an inert carrier. Due to their ability to incorporate or sorb organic and inorganic compounds and/or solutions of various solutes in aqueous or organic solvents within their matrix and release these sorbed agents to their surrounding environment under a wide variety of conditions, they have wide utility in the field of agriculture. The active agents such as fertilizers, herbicides and so forth, are not chemically affected by nor do they react in any significant manner with the crosslinked polymeric materials. The polymeric materials disclosed herein provide a more effective means for achieving the known functions of water and other known active agents or agricultural chemicals.

WHAT IS CLAIMED IS:

1. A process for chemically crosslinking polyethers which comprises contacting said polyethers with a divinyl monomer in the presence of a free radical catalyst.

2. A process for chemically crosslinking polyethers which comprises grafting a divinyl substituent of a divinyl monomer to a carbon atom adjacent an oxygen atom in the polyether chain of a polyether in the presence of a free radical catalyst.

3. A process for chemically crosslinking poly-(ethylene oxide) which comprises contacting poly(ethylene oxide) with a divinyl monomer in the presence of a free radical catalyst.

4. A process for chemically crosslinking poly-(ethylene oxide) which comprises contacting poly(ethylene oxide) with methylenebisacrylamide in the presence of azobisisobutyronitrile.

5. A crosslinked polyether prepared as in claim 1.

6. A crosslinked poly(ethylene oxide) prepared as in claim 4.

